

Modeling for Organic Conduction

Recently, there has been increased interest in molecular electronics due to the prospect of designing efficient electronic nano-scale components that could exhibit functionalities not achievable with silicon devices (e.g. optical emitters). Despite the significant progress made in the development of techniques to fabricate and characterize molecular conductors, the fact remains that molecular electronics is currently more of an art than a science characterized by a significant lack of reproducibility. The scientific and technological objective of this project is to evaluate/develop theoretical and computational tools that model the electrical activity and transport properties of organic molecules used in nanoelectronic devices.

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The decrease in the size of transistors by a factor of two every eighteen months, the trend known as Moore's law, has led to the fabrication of microelectronic devices that are increasingly faster, more powerful, and ubiquitous. However, it is projected that the physical limits of even the most advanced lithographic techniques under development will be reached in the foreseeable future. Beyond that time, continued increases in circuit density will require a paradigm shift in the design, make-up, fabrication, and operation of electronic components. Molecular electronic is seen by many as a viable alternate component technology. Molecules, either singly or in small ensembles, perform the function of the electronic components. Significant progress has taken place in the field. Molecular field-effect transistors (IBM, Lucent), reversible molecular switches (Hewlett-Packard), molecular negative-differential resistors (MEC, Inc), and molecular rectifying-diode have all been discovered and characterized, and Hewlett-Packard recently announced a prototype molecular-memory device with a density of ~ 10 GBits/cm². Despite this progress, it has become clear that there is a marked need for the development of robust theoretical and experimental tools that could be used on a routine basis in the design of novel materials leading to the development of reliable electronic devices based on molecular electronics. In this project, reliable and efficient theoretical methodologies leading to the understanding of the fundamental mechanisms governing electrical conductance in organic materials at the molecular level are developed and compared to experimental data. Theoretical studies of the electronic transport of

molecular wire circuits are conducted using a time-independent Landauer scattering formalism based on a first-order expansion of the system non-equilibrium Green's function (NEGF). In this model, the molecular bridge is bound to the metallic electrodes by means of thiolate groups at the head and tail of the bridge. Possible effects of the system's chemical stability, conformational changes of the organic conductor, and excited states on the transport properties of the device are also investigated. In addition, methods to predict the effects of electrostatic interactions at the molecule-electrode junction on the Current-Voltage curve are currently being examined. These effects could lead to technologically important phenomena such as molecular rectification and negative differential resistance. In this research, a simple methodology to study trends in conductance of molecule-metal junctions based on Density Functional Theory calculations (DFT) of modified quasi-molecular Green functions in a capacitor-like electric field was developed. This method, called the *Green Function Condensed-to-Fragments* model (GFCF), is based on a series of assumptions about the voltage spatial profile and the molecule-surface chemisorptive coupling in metal-molecule interfaces that seem to be validated for a number of junctions. The method assumes that the voltage drops entirely at the interfaces and that the junction conductance can be approximately factorized as a product of contact and molecular contributions. The main advantage of this approximate methodology rests on the fact that it is very simple to use, computationally efficient, and its results can be analyzed in terms of familiar chemical concepts such as molecular orbitals and dipole moments. The model has been used in the calculation of I-V curves of a series of the π -conjugated oligomers: 4-phenylethynyl-1-[(4-thiol)-phenyl-ethynyl] benzene (OPE), 2-amino-5-nitro-4-phenylethynyl-1-[(4-thiol)-phenylethynyl] benzene (NH₂-OPE-NO₂), and 2-fluoro-4-phenylethynyl-1-[(4-thiol)phenylethynyl]benzene (F-OPE). The results of these calculations were compared to the corresponding experimental I-V curves. These three oligo(phenylene-ethynylene)s are highly conjugated systems with similar electronic structure, and possible differences in their conductance behavior should be only the result of substitution in the central ring. The results obtained in this work indicate that the I-V curves exhibited by substituted π -conjugated oligomers attached to gold electrodes can be interpreted qualitatively with the help of the quasi-Green function matrix projected onto fragments of the isolated molecule. This conclusion is supported by the reasonable qualitative agreement between the computed and experimental I-V curves in the case of OPE, F-OPE, and NO₂-OPE-NH₂, especially at voltages lower than 1.3 V (see Fig. 1).

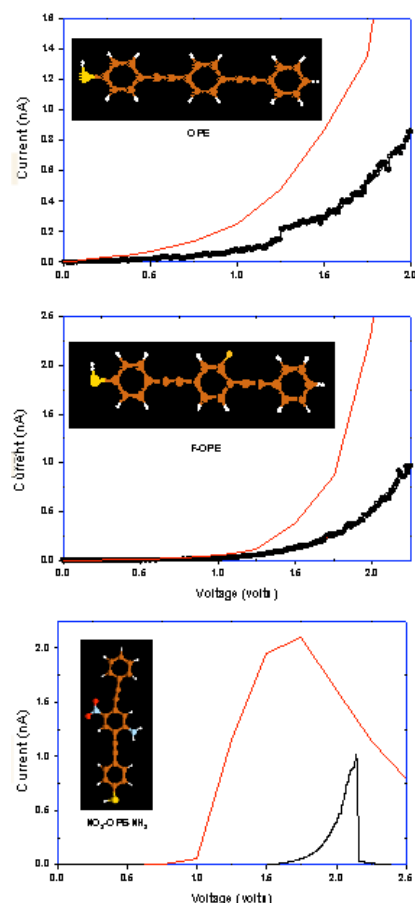


Figure 1: Comparison of theoretical (red line) and experimental (black dots) I-V curves for OPE's.

A similar qualitative agreement in the case of saturated hydrocarbons such as C₁₂H₂₅SH, oligo(phenylene vinylenes) as well as in a series of substituted platinum(II) acetylides indicates that the GFCF method is transferable to different molecular systems and that its reliability just depends on the voltage spatial profile of the system. The discrepancies between the theoretical and experimental I-V curves observed at larger voltages can be attributed to limitations of the method in this voltage regime. However, it is very encouraging to see that even at these voltages the simple theoretical scheme used here predicts the right trends for the three molecules studied. The results of our calculations lead to the conclusion that the I-V switching observed in NO₂-OPE-NH₂ correlates well with significant rearrangements in the electronic structure of the molecule (mainly through the pz atomic orbitals) reflected in the behavior of the corresponding Green functions with the voltage. In the case of OPE and F-OPE these drastic changes are not observed and the systems behave as simple molecular tunneling wires. The results of this research pose the possibility of using standard quantum-chemical calculations as a “screening tool” to aid in the rational design of

other molecular systems that could exhibit novel and technologically important I-V behavior. We are currently testing the reliability and transferability of the model on a larger variety of molecular systems for which reliable experimental data is available.

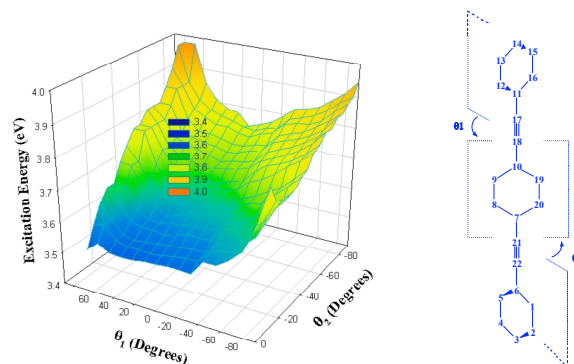


Figure 2: Changes in the excitation energy of OPE as a function of the ring torsion angles..

We are also investigating the nature of the interaction between the molecule and the metal at the interface. In particular, we are applying highly correlated *ab initio* molecular orbital theory in order to determine possible changes in the electronic structure of the molecule due to chemisorption to the metallic surface. Properties such as geometrical parameters, chemical stability, binding energies and UV-vis spectra (see Figure 2) have been computed and the results compared to available experimental data.

This research is conducted within the recently established NIST Center for Theoretical and Computational Nanosciences. Within the context of this center it is envisioned that the theoretical models developed and validated in this work will provide a set of important tools that will complement the experimental studies conducted by researchers in the nascent molecular electronics industry as well as in research centers at NIST, National Labs and Universities.

For More Information on this Topic

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